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STIGMASTEROLS FROM *TYPHA LATIFOLIA*[1]

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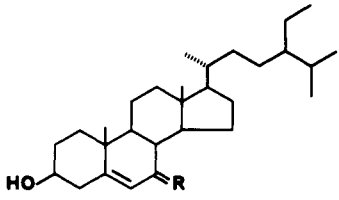
ABSTRACT.—Several free and acylglucosylated stigmasterols have been isolated from the aquatic plant *Typha latifolia*. The structures of three novel acylglucosylsterols have been assigned on the basis of spectroscopic data and by chemical modification studies.

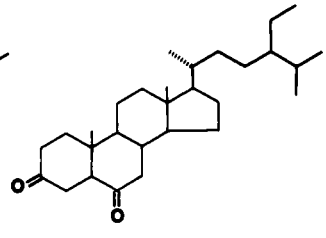
Typha latifolia L. (Typhaceae) is a widespread diffused aquatic plant we are studying in connection with its potential antialgal activity (1). Glycosylflavonols (2), carotenoid-like compounds (3), and novel sterols with the ergostane (4) and noreburicane (5) skeletons have already been isolated from this species, and in this paper we report the isolation and characterization of several free and acylglucosylated sterols with the stigmastane skeleton.

The free stigmasterols were isolated from the ethereal extract of the plant: besides β-sitosterol [**1**], compounds **2–9** variously oxidized in the A and B rings were characterized. The structures were assigned on the basis of their uv, ms, ^{1}H- (Table 1) and ^{13}C-nmr (Table 2) data. Even though high field nmr studies have not been reported, 7-oxositosterol [**2**], 7β-hydroxysitosterol [**3**], and 7α-hydroxysitosterol [**4**] have been described (6) as well as enone **6** (7), dione **5**, and enedione **7** (8). ^{1}H- and ^{13}C-nmr chemical shifts of these compounds were assigned mainly on the basis of previously reported data for analogous cholestane and androstane steroids (9,10) and by comparison with the data of β-sitosterol.

Hydroxyenone **8** showed a molecular ion at *m/z* 428 in its eims spectrum, consistent with a composition $C_{29}H_{48}O_2$. The presence of hydroxyl and enone functions was revealed by strong absorptions at 3570, 1675, and 1640 cm^{-1} in the ir spectrum and confirmed by a strong absorption at 238 nm in the uv spectrum. Its ^{1}H-nmr spectrum showed an olefinic proton as a singlet at δ 5.82 and a proton geminal with the hydroxyl group as a narrow signal at δ 4.34, as well as three methyl doublets at δ 0.81, 0.84, 0.92, a methyl triplet at δ 0.85, and two methyl singlets at δ 0.74 and 1.37. A comparison with β-sitosterol suggested that both compounds had the same side chain, while the shape of the olefinic and carbinyl protons suggested the presence of a β-axial hydroxyl group at C-6. Thus, the H-19 methyl group was shifted 0.2 ppm downfield in **8** compared with **6**, owing to 1,3 diaxial interaction with the hydroxyl group (11). ^{13}C-



1 R=H_2
2 R=O
3 R=H, β-OH
4 R=H, α-OH



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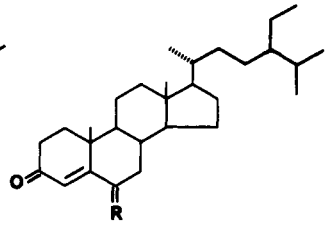


6 R=H_2
7 R=O
8 R=H, β-OH
9 R=H, α-OH

[1]Part XVI in a series of studies on aquatic plants. For part XV, see Della Greca *et al.* (3).

TABLE 1. ^{1}H-nmr Chemical Shifts (δ) of Stigmasterols.[a]

Proton	Compound								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
H-3	3.52 m	3.69 m	3.56 m	3.59 m	—	—	—	—	—
H-4	—	—	—	—	—	5.74 d (2.2)	6.18 s	5.82 s	6.20 d (1.8)
H-6	5.35 m	5.70 d (1.7)	5.30 s	5.62 d (4.8)	—	—	—	4.34 m	4.32 m
H-7	—	—	3.86 d (4.4)	3.86 m	—	—	—	—	—
H-18	0.69 s	0.69 s	0.70 s	0.69 s	0.70 s	0.72 s	0.73 s	0.75 s	0.72 s
H-19	1.01 s	1.20 s	1.05 s	0.99 s	0.96 s	1.19 s	1.17 s	1.38 s	1.19 s
H-21	0.92 d (6.4)	0.93 d (6.5)	0.93 d (6.6)	0.93 d (6.6)	0.93 d (6.4)	0.93 d (6.6)	0.94 d (6.5)	0.93 d (6.5)	0.93 d (6.5)
H-26	0.83 d (6.8)	0.84 d (6.5)	0.85 d (6.6)	0.83 d (6.7)	0.84 d (6.0)	0.84 d (6.8)	0.84 d (6.1)	0.84 d (6.1)	0.85 d (6.0)
H-27	0.81 d (6.9)	0.82 d (6.7)	0.81 d (6.7)	0.82 d (6.7)	0.82 d (6.6)	0.82 d (6.8)	0.82 d (6.4)	0.82 d (6.1)	0.82 d (6.1)
H-29	0.85 t (7.8)	0.85 t (7.1)	0.85 t (7.2)	0.85 t (7.2)	0.85 t (6.9)	0.85 t (7.2)	0.85 t (6.9)	0.85 t (6.7)	0.86 t (6.8)

[a]Apparent coupling constants in Hz are reported in parentheses.

nmr assignments were based on the values of the chemical shifts of enone **6**, corrected for the presence of a β hydroxyl group at C-6 (12), and were confirmed by H-C COSY.

The stereoisomeric 6α-hydroxy enone **9** showed the H-4 proton shifted downfield at δ 6.20, due to the spatial proximity of the 6-OH group, the H-19 methyl at δ 1.19 as in enone **6**, and the H-6 as a broad multiplet at δ 4.32 due to its β-axial orientation. The different stereochemistry at C-6 caused an upfield shift of the C-4, C-5, and C-6 carbons and a downfield shift of C-8 and C-10 in the ^{13}C-nmr spectrum.

Recently Khan and Malik (13) reported the spectroscopic characterization of (24*S*)-24-ethylstigmast-4-en-6α-ol. Strangely, the ^{1}H-nmr chemical shifts reported by these authors closely resemble those of 6β-hydroxyenone **8** and are quite different from those of the 6α isomer **9**, even though the positions of the H-4 and H-6 protons correspond to those of the latter. Also ^{13}C-nmr data are in agreement with those of **8**, excepting the chemical shift of C-8. Finally, the data of the Jones oxidation product of their hydroxyenone are different from those of enedione **7**.

The oxidation pattern of the stigmasterols corresponds to that obtained by microbiological oxidation of cholesterol (14), thus suggesting the presence in *T. latifolia* of an enzymic system able to transform β-sitosterol [**1**] into sterols **2–9**. However, the possibility that **3**, **4** and **8**, **9** are artifacts arising from β-sitosterol and stigmast-4-en-3-one, respectively, through an autoxidation process (15) cannot be ruled out.

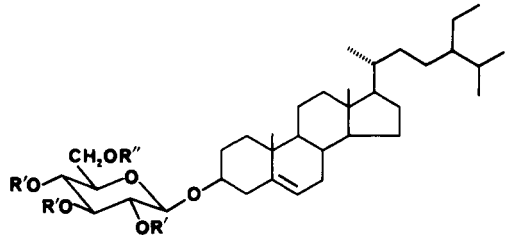
TABLE 2. ^{13}C-nmr Chemical Shifts (δ) of Stigmasterols.

Carbon	Compound								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
C-1 . .	37.33	36.62	36.93	37.00	38.05	35.68	35.51	37.06	36.25
C-2 . .	31.63	31.18	31.56	31.37	39.38	33.89	33.95	34.22	34.14
C-3 . .	71.73	70.52	71.42	71.35	209.11	198.92	199.48	200.11	202.94
C-4 . .	42.20	41.79	41.71	42.01	37.01	123.64	125.42	126.26	119.42
C-5 . .	140.71	169.35	143.48	143.88	57.54	171.01	161.06	168.55	157.78
C-6 . .	121.63	126.13	125.42	123.86	211.27	32.86	202.31	73.22	68.67
C-7 . .	31.96	204.21	73.34	65.36	46.64	32.07	46.79	38.56	39.36
C-8 . .	31.81	45.39	40.91	37.51	37.40	35.73	39.11	29.70	33.76
C-9 . .	51.13	50.02	48.26	42.26	53.84	53.84	50.97	53.61	53.74
C-10 . .	36.43	38.24	36.42	37.39	41.25	38.58	34.19	37.97	39.30
C-11 . .	21.09	21.20	21.06	20.71	21.66	21.03	20.85	20.95	21.00
C-12 . .	39.79	39.68	39.54	39.17	38.05	39.48	39.80	39.58	39.44
C-13 . .	42.37	41.79	42.91	42.13	42.98	42.35	42.51	42.49	41.51
C-14 . .	56.75	49.93	55.37	49.42	55.99	55.94	55.84	55.87	55.54
C-15 . .	24.15	26.30	26.36	25.90	24.02	24.12	23.95	24.12	24.14
C-16 . .	28.25	28.53	28.51	28.31	28.05	28.10	27.99	28.14	28.08
C-17 . .	56.02	54.69	55.95	55.70	56.61	56.08	56.53	56.05	55.96
C-18 . .	11.84	11.87	11.79	11.63	12.55	11.98	11.95	11.98	11.89
C-19 . .	19.46	17.28	19.12	18.25	12.05	17.38	17.48	19.46	17.95
C-20 . .	36.07	36.06	36.07	36.10	36.05	36.10	36.01	36.08	36.06
C-21 . .	18.68	18.90	18.81	18.80	18.69	18.72	18.69	18.70	18.66
C-22 . .	33.95	33.93	33.97	33.91	33.81	34.01	33.81	33.88	33.85
C-23 . .	26.10	26.07	26.11	25.97	26.06	25.99	26.03	26.09	26.09
C-24 . .	45.82	45.80	45.84	45.82	45.77	45.80	45.79	45.81	45.82
C-25 . .	29.15	29.11	29.14	29.12	29.13	29.11	29.12	29.15	29.16
C-26 . .	19.77	19.77	19.77	19.81	19.81	19.81	19.79	19.77	19.75
C-27 . .	19.21	19.01	19.00	19.02	19.00	19.18	18.99	19.00	18.99
C-28 . .	23.13	23.04	23.05	23.06	23.07	23.10	23.05	23.06	23.06
C-29 . .	11.04	11.95	11.95	11.99	12.00	11.14	11.87	11.98	11.89

Sequential cc of the MeOH extract followed by preparative tlc gave an inseparable mixture of acylglucosylsterols **10a–13a**. On the basis of its spectral data, the mixture was thought to consist of compounds characterized by the same glycosylsterol moiety bearing different acyclic chains at the C-6′ position of the glycosyl unit.

The ir spectrum of the mixture showed the presence of hydroxylic and ester carbonyl groups; the ^{1}H-nmr spectrum, beside signals that agreed with those of β-sitosterol, showed the anomeric H-1′ proton of the β-glycosidic unit as a doublet at δ 4.39 (J = 7.7 Hz) and the H-6′ methylene as two double doublets centered at δ 4.25 (J = 12.1 and 2.2 Hz) and 4.52 (J = 12.1 and 5.3 Hz), while the remaining protons were partially overlapped in the 3.2–3.8 ppm range. Finally olefinic protons at δ 5.36, allylic methylenes at δ 2.08 and 2.79, long chain methylenes at δ 1.26, and other signals in the high field of the spectrum attributable to saturated and unsaturated acylic chains were detected in an indefinite ratio. The ^{13}C-nmr spectrum confirmed the presence of β-sitosterol and indicated β-D-glucose as the sugar moiety owing to the presence of signals at δ 101.25, 76.33, 76.25, 74.00, 70.52, and 63.44 (16). Several carbons of saturated and unsaturated acyclic residues were also present. The downfield shift of C-6′, as well as the corresponding downfield shift of H-6′, suggested that the acyclic chains were linked at this position.

When the mixture of **10a–13a** was acetylated with Ac_2O in dry pyridine, argentation preparative tlc allowed the separation of the derivatives **10b–13b**. The ^{1}H-nmr spectrum of the most abundant compound **10b** showed, besides the signals of β-sitosterol, β-D-glucose, and three acetate methyls, six further olefinic protons overlapping that of β-sitosterol, two allylic methylenes at δ 2.08, two methylenes α to two double bonds at δ 2.79, four methylenes at δ 1.26, methylenes α and β to the carboxyl group at δ 2.30 and 1.61, respectively, and finally a methyl triplet at δ 0.98 which collapsed into a singlet by irradiation at δ 2.08. The ^{13}C-nmr spectrum showed signals in good agreement with those reported for β-sitosterol with the exception of C-2, C-3, and C-4, which were shifted to δ 29.33, 74.05, and 38.94, respectively, by the presence of the glucosidic moiety at C-3. Besides the glucose carbons at δ 101.08, 72.56, 71.35, 70.88, 68.10, and 61.60, signals were also present attributable to a triunsaturated C_{18} acyclic residue with a carbonyl carbon at δ 173.53, six olefinic carbons at δ 131.88, 130.17, 128.41, 128.32, 127.94, and 127.28, four allylic methylene carbons at δ 27.33, 25.76, 25.68, and 20.68, six methylenes at δ 34.19, 29.72, 29.30, 29.26, 29.21, and 24.79, and a methyl carbon at δ 14.31. These signals, as well as those of the acyclic chains of **11b** and **12b**, were assigned by comparison with the data reported for analogous fatty acid methyl esters (17).



10a R′=H, R″=octadeca-(9*Z*,12*Z*,15*Z*)-trienoyl
10b R′=Ac, R″=octadeca-(9*Z*,12*Z*,15*Z*)-trienoyl
11a R′=H, R″=octadeca-(6*Z*,9*Z*,12*Z*)-trienoyl
11b R′=Ac, R″=octadeca-(6*Z*,9*Z*,12*Z*)-trienoyl
12a R′=H, R″=octadeca-(9*Z*,12*Z*)-dienoyl
12b R′=Ac, R″=octadeca-(9*Z*,12*Z*)-dienoyl
13a R′=H, R″=octadecanoyl
13b R′=Ac, R″=octadecanoyl

Saponification of **10b** gave a fatty acid that was esterified with ethereal CH_2N_2. Glc comparison with an authentic sample indicated that the octadeca-(9*Z*,12*Z*,15*Z*)-trienoyl residue was present in **10b**.

^1H- and ^{13}C-nmr spectra of **11b** were rather similar to those of **10b**, showing only minor differences in the chemical shifts of carbons of the acyclic chain. Glc of the fatty acid methyl ester obtained by saponification of **11b** indicated the presence of the isomeric octadeca-(6*Z*,9*Z*,12*Z*)-trienoyl residue.

Spectroscopic data of **12b** and **13b** confirmed the common presence of 3-*O*-β-glucopyranosyl-stigmast-5-ene with acetate groups at C-2′, C-3′, and C-4′ and showed that the side chain of **12b** contained only two olefinic moieties whereas **13b** had a saturated acyclic residue. Glc of the fatty acid methyl esters obtained by saponification and esterification indicated that an octadeca-(9*Z*,12*Z*)-dienoyl residue was in **12b** and an octadecanoyl one in **13b**.

Acylglucosylsterols have already been isolated from several plant sources. In *Cucumis sativus* (18), compounds contained β-sitosterol, stigmasterol, and stigmastanol as sterols and palmitate and stearate as acylic residues. These lipid residues were also found in acylglucosylsterols from *Alisma plantago-aquatica* (19) and *Momordica charantia* (16); in this respect the isolation from *Typha latifolia* of metabolites with a high degree of unsaturation in the acyclic chains is of interest.

EXPERIMENTAL

PLANT MATERIAL.—The plants of *Typha latifolia* were collected in a ditch near Naples. A voucher specimen is on deposit at the botanical garden of the University of Naples.

GENERAL EXPERIMENTAL PROCEDURE.—^1H- and ^{13}C-nmr spectra were obtained on a Bruker AM 400 spectrometer equipped with a dual probe (H/C 400.1/100.6) in $CDCl_3$ solutions. H-C COSY were performed with the Bruker XHCORR microprogram using a delay $D_3 = 3.6$ ms (corresponding to $J_{C,H}$ 140 Hz). Ms spectra were recorded at 70 eV on Kratos MS 80 and MS 50 spectrometers. Uv spectra were recorded on a Perkin-Elmer LAMBDA 7 spectrophotometer. The chromatographic glc apparatus consisted of a capillary column chromatograph FRACTOVAP 4160 (Carlo Erba) equipped with a Varian 4270 integrator. An OV-1 column (25 m × 0.32 mm i.d., film thickness 0.1–0.15 μm) with a column temperature of 180° was used for fatty acid methyl esters analysis with authentic samples purchased from ALLTECH Associates.

ISOLATION OF FREE STEROLS.—The ethereal extract of *T. latifolia* (8.5 g) was washed with 2 N aqueous NaOH to eliminate acidic components and then neutralized and evaporated in vacuo to give neutral material (6.3 g) which was directly chromatographed on a Si gel column. Crude enone **6** was eluted with hexane-Et_2O (19:1), diones **7** and **5** and β-sitosterol [**1**] with hexane-Et_2O (9:1), hydroxyenones **8**, **2**, and **9** with hexane-Et_2O (4:1), and finally diols **4** and **3** with hexane-Et_2O (1:1).

Stigmast-4-en-3-one [**6**].—Crude **6** (49 mg), after purification by preparative tlc [C_6H_6-Et_2O (17:3)] had ms *m/z* 412, 397, 271; uv λ max (hexane) 231 nm (log ε 4.24).

Stigmast-4-en-3,6-dione [**7**], *stigmastan-3,6-dione* [**5**], *and* β-*sitosterol* [**1**].—The mixture was separated through preparative plc [hexane-EtOAc (4:1)]. Compound **7** (49 mg): ms *m/z* 426, 411, 285; uv λ max (EtOH) 250 nm (log ε 4.24). Compound **5** (56 mg): ms *m/z* 428, 413, 287; uv λ max (EtOH) 286 (log ε 1.73). Compound **1** (512 mg): ms *m/z* 414, 399, 396, 273.

*Stigmast-4-en-6*β *-ol-3-one* [**8**], *3*β-*hydroxystigmast-5-en-7-one* [**2**], *and* 6α-*hydroxystigmast-4-en-3-one* [**9**].—The mixture was chromatographed on preparative tlc [$CHCl_3$-EtOAc (9:1), 2 runs]. Compound **8** (85 mg): ms *m/z* 428, 413, 410, 287; uv λ max (EtOH) 238 nm (log ε 4.11). Compound **2** (22 mg): ms *m/z* 428, 413, 410, 287; uv λ max (EtOH) 239 nm (log ε 4.10). Compound **9** (31 mg): ms *m/z* 428, 413, 410, 287; uv λ max (EtOH) 243 (log ε 4.21).

*Stigmast-5-ene-3*β,*7*α-*diol* [**4**] *and stigmast-5-ene-3*β,*7*β-*diol* [**3**].—The mixture of **4** and **3** was rechromatographed on Si gel eluting with $CHCl_3$-EtOAc (19:1) and then separated into its components through preparative plc [C_6H_6-EtOAc (7:3) 3 runs]. Compound **4** (4 mg): ms *m/z* 430, 415, 412, 394, 289. Compound **3** (7 mg): ms *m/z* 430, 415, 412, 394, 289.

ISOLATION OF ACYLGLUCOSYLSTEROLS.—The MeOH extract of *T. latifolia* (85 g) was distributed

between H_2O and EtOAc. The organic layer, after evaporation of the solvent, gave a residue (4.1 g) which was directly chromatographed on a Si gel column (100 g). $CHCl_3$-Me_2CO (7:3) gave a complex mixture (1.2 g) which was rechromatographed on Si gel (120 g). The material eluted with $CHCl_3$-Me_2CO (7:3) (300 mg) was purified by preparative Si gel tlc [$CHCl_3$-Me_2CO (7:3), 3 runs] to give a mixture of **10a–13a** (210 mg), which was acetylated with Ac_2O (0.5 ml) in dry pyridine (5 ml) at room temperature. The mixture of acetyl derivatives **10b–13b** was resolved through preparative argentation tlc [hexane-EtOAc (4:1)] into its pure components **10b** (80 mg), **11b** (35 mg), **12b** (27 mg), and **13b** (33 mg).

Compound **10b**.—^{1}H nmr δ 5.36 (m, H-6, H-9″, H-10″, H-12″, H-13″, H-15″, H-16″), 5.21 (dd, J = 9.5 and 9.5 Hz, H-3′), 5.06 (dd, J = 9.5 and 9.5 Hz, H-4′), 4.96 (dd, J = 9.5 and 8.1 Hz, H-2′), 4.59 (d, J = 8.1 Hz, H-1′), 4.24 (dd, J = 12.1 and 5.3 Hz, H-6′), 4.12 (dd, J = 12.1 and 2.2 Hz, H-6′), 3.67 (m, H-5′), 3.49 (m, H-3), 2.79 (dd, J = 6.9 and 7.3 Hz, H-11″, H-14″), 2.30 (t, J = 7.3 Hz, H-2″), 2.08 (m, H-8″, H-16″), 2.05, 2.03, 2.01 (sss, OAc), 1.62 (m, H-3″), 1.26 (m, H-4″, H-5″, H-6″, H-7″), 1.01 (s, H-19), 0.98 (t, J = 7.3 Hz, H-18″), 0.92 (d, J = 6.4 Hz, H-21), 0.85 (t, J = 7.8 Hz, H-29), 0.83 (d, J = 6.8 Hz, H-26), 0.81 (d, J = 6.9 Hz, H-27), 0.69 (s, H-18).

Compound **11b**.—^{13}C nmr δ 173.66 (C-1″), 130.43 (C-13″), 129.62 (C-6″), 128.45 (C-10″), 128.36 (C-7″), 128.15 (C-9″), 127.71 (C-12″), 33.99 (C-2″), 31.65 (C-16″), 29.47 (C-15″), 29.21 (C-4″), 27.35 (C-14″), 26.94 (C-5″), 25.75 (C-11″), 25.70 (C-8″), 24.67 (C-3″), 22.64 (C-17″), 14.05 (C-18″).

Compound **12b**.—^{1}H nmr δ 5.36 (m, H-9″, H-10″, H-12″, H-13″), 2.79 (dd, J = 6.9 and 7.2 Hz, H-11″), 2.08 (m, H-8″, H-14″), 1.26 (m, H-4″, H-5″, H-6″, H-7″, H-15″, H-16″, H-17″), 0.84 (m, H-18″).

Saponification of **10b–13b**.—Aliquots (10 mg) of pure compounds were dissolved in $CHCl_3$-MeOH-10 M NaOH (2:7:1) (3 ml) and kept at 60° for 1 h. Usual workup gave fatty acids which were esterified with CH_2N_2.

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